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SYNTHESIS AND CHEMISTRY OF ENERGETIC  
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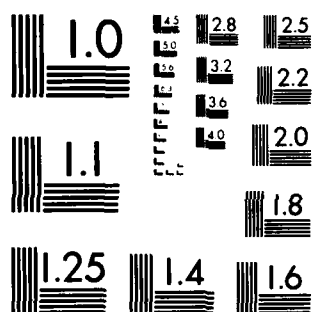
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)  <b>New approaches to the synthesis of metallotetraazadienes are described. These include reactions between organic azides and transition metal carbonyl complexes, as well as reactions between metal halide complexes and dilithiated tetrazenes. Attempts to prepare disubstituted tetra- zenes by the oxidation of unsymmetrical blocked hydrazines is described. The preparation of super reduced metallotetraazadienes has also been achieved.</b>		

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Final Scientific Report (12/1/82-9/31/83)

Synthesis and Chemistry of Energetic

Metallotetraazadienes

Grant AFOSR-83-0021

Principal Investigator - William C. Trogler

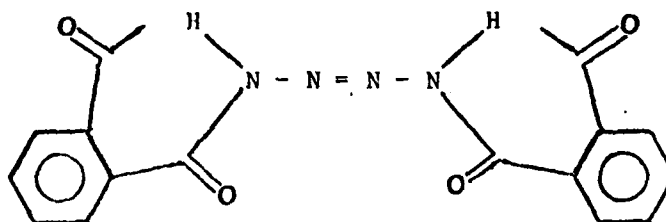


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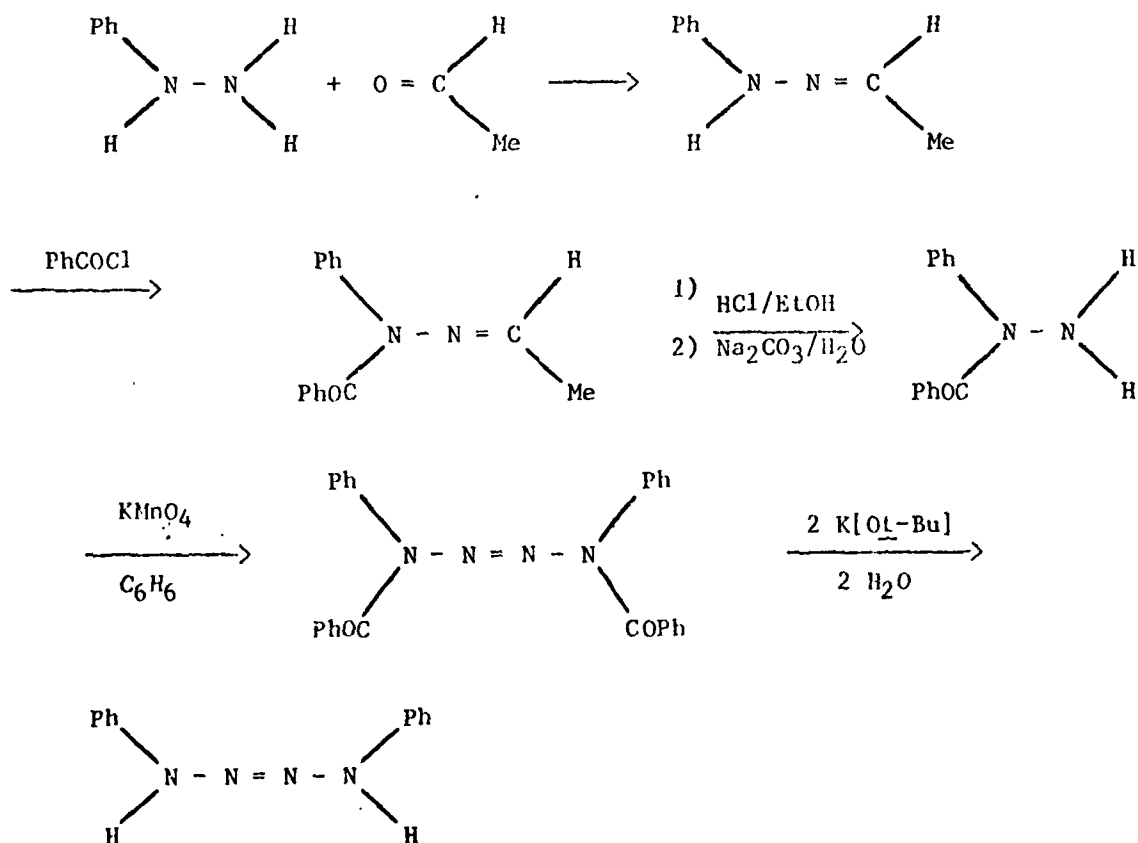
Several new tetraazadiene complexes have been prepared and new avenues for their preparation are under investigation.

I) Products derived from organic azide reactions. The sterically hindered azide 2,6-dimethylazide, is readily synthesized from 2,6-dimethyl aniline. It has the advantage of being relatively nonexplosive (28% N) compared to simple alkyl and aryl azides. Furthermore, in reactions with  $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2$  the yield of metallotetraazadiene complex is very high (85-90%). This has enabled the preparation of large (5g) quantities of metallotetraazadienes, which permits a more complete study of their chemistry and physical properties. We have discovered that complexes of the type  $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{RN}_4\text{R})$ , where R = 2,6- $(\text{CH}_3)_2\text{C}_6\text{H}_3$ ,  $\text{CH}_3$ ,  $\text{C}_6\text{H}_5$ , 2,4- $\text{F}_2\text{C}_6\text{H}_3$ , and  $\text{C}_6\text{F}_5$  can be reduced by both chemical (Na/Hg in THF) and electrochemical methods; the spectroscopic properties (UV-VIS and epr) of the radical anions correlate well with those expected if the acceptor orbital is a  $\pi^*$  level delocalized over the unsaturated  $\text{MN}_4$  ring. Super-reduced complexes can be isolated in pure form by carrying out the chemical reductions in the presence of dibenzo-18-crown-6 to stabilize the sodium cation. The above research is in the process of being prepared for publication. We are also exploring the reactions of organic azides with  $\text{V}(\text{CO})_6$  and  $\text{V}(\eta^5\text{-C}_5\text{H}_5)_2$ .

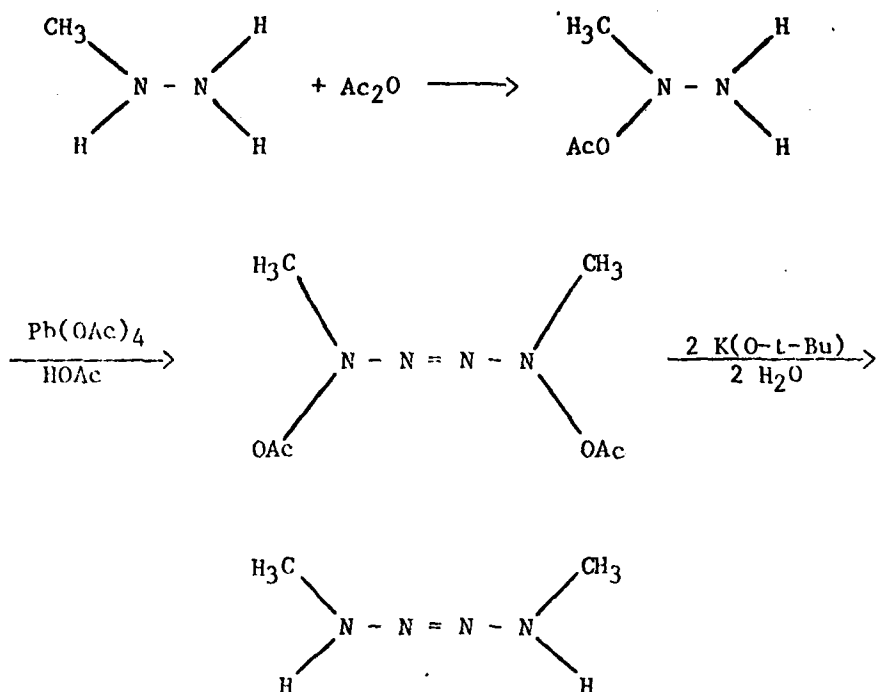
II) Organic tetrazene chemistry. In order to preform the tetraazadiene ligand, we are attempting the synthesis of  $\text{LiN(R)NNN(R)Li}$  reagents. The precursor to the latter reagent would be  $\text{HN(R)NNN(R)H}$ . Although the synthesis of tetraalkyltetrazenes is well known, the preparation of the disubstituted derivatives presents an an interesting challenge. We repeated a recent Wiberg preparation of  $\text{Li}(\text{SiMe}_3)\text{N=N=N-N}(\text{SiMe}_3)\text{Li}$ ; however, the actual yields are considerably less than reported. The disubstituted tetrazene (easily obtained from



phthalimide) has been prepared, and we have been able to deprotonate this compound with two equivalents of BuLi. Above  $-78^{\circ}\text{C}$  nucleophilic attack occurs at the carbonyls. To avoid this complication we are engaged in the synthesis of the phenyl analogue by the route



This synthesis is complete up to the unsymmetrical acylated hydrazine. An alternative procedure for the methyl derivative is being investigated.



We are confident that disubstituted tetrazenes can be made since the phthalimide derived compound was stable, and the dianion could be generated. If we can prepare the dimethyltetrazene compound, it may actually be of immediate interest as a propellant since the C/N ratio would be more favorable than for unsymmetrical dimethyl hydrazine (it might also still be a liquid).